175. *A Volumetric Determination of the Atomic Weight of Terbium.*

By JOSEPH K. MARSH.

THE present accepted value for the atomic weight of terbium (159·2) rests solely on Urbain's determination (*Compt. rend.*, 1906, **142**, 957) of the ratio of the anhydrous sulphate to the octahydrate.

The preparation of pure terbium material by fractionation of the dimethylphosphate has already been described (Marsh, J., 1934, 1972). This material has now been used in determining the ratio $Tb_2O_3 : 3C_2O_3$ by ignition of the oxalate and by titration with standard permanganate. The value derived for the atomic weight is 158·9.

Preparation of Materials.—Nitric acid distilled from silver was redistilled from resistance glass, and the middle fraction taken; 10 ml. on evaporation gave no weighable residue. Terbium peroxide was dissolved in this acid, and the solution diluted to contain 1 g. in 50 ml. and *N*/2 concentration of free acid. Reagent oxalic acid was twice crystallised from dilute nitric acid; 5 g. on slow sublimation gave no weighable residue. A hot 10% oxalic acid solution was added slowly to the hot terbium nitrate solution, with vigorous stirring, till in slight excess. The reaction mixture was kept on the water-bath for several hours till the precipitate had become more granular. The bulk of the liquid was then decanted and treated with half its volume of 10% oxalic acid; on cooling, crystals of terbium oxalate up to 1 mm. long separated, but as these were troublesome to dissolve during the permanganate titration, they were kept apart. The oxalate was collected in a Jena-glass funnel, and washed back into a beaker three times. Finally, it was washed in the funnel with a little alcohol, spread on a clock glass, dried at 30°, and kept protected from dust but freely exposed to the air for 2 days with occasional mixing. It was then thoroughly mixed and stored in a stoppered bottle.

Density of Terbium Oxalate.—Two or three large crystals about 1 mm. long were selected, and a bromoform–chloroform mixture prepared in which they remained suspended. The density found was 2·60.

Density of Terbium Oxide.—About 3·8 g. were placed in a 5 ml. density bottle and covered with hot, air-free water. The bottle was then placed in a vacuum desiccator, and the water cautiously boiled under reduced pressure till all entangled air was extracted. The density thus found was 7·68.

Ignition of Terbium Oxalate.—This was done in transparent silica crucibles in an electric furnace. The crucibles were ground flat at the top and the lids were similarly ground so that when they were in place the crucibles were practically air-tight, and their contents protected from assimilation of carbon dioxide and moisture. Heating the oxalate from room temperature to dull red occupied 2 hours. Not much apparent change took place below 350°, but shrinkage and darkening then began, and the rate of heating was reduced. After a time, the temperature was quickly raised to 1000° and maintained for 5 hours. The crucible was wholly or largely uncovered, and the furnace not too tightly closed to allow of ready escape of carbon dioxide. The dark brown peroxide thus formed was next reduced in a stream of hydrogen in a circular iron box placed in the electric furnace. Reduction occurred at a dull red heat, but a temperature of 700—800° was employed for 1/4 hour. Cooling was hastened by quenching in water, and if the contents were white the crucible was quickly transferred to a desiccator, and weighed after 40—60 minutes. The results are tabulated below :

Oxalate, g.	0·8046	1·16364	1·33993	1·27706	1·14461
Oxide, g.	0·38337	0·55446	0·63838	0·60848	0·54333
Oxide, %	47·655	47·649	47·643	47·647	47·644
					Mean 47·648

Weighings throughout have been corrected to vacuum standard.

Determination of Oxalate Radical.—Sørensen's sodium oxalate (Riedel Haën A.-G.) was used to standardise *N*/10-potassium permanganate. An aqueous solution of 20 ml. of concentrated sulphuric acid and 1 g. of manganese sulphate per litre was boiled till air-free and then treated with potassium permanganate. 5 L. caused rapid decolorisation of a few drops, but later, disappearance of colour occurred only after several minutes, and finally a single drop caused a permanent tint distinctly visible in 5 l. but not in 250 ml. 250 Ml. of this solution were used in each titration to dissolve the oxalate. A 50 ml. burette with N.P.L. certificate of corrections was used. Small weighing vessels of about 1 ml. capacity were made from the bottoms of specimen tubes. These with their contents were dropped into the titration liquid, and standard practice followed.

The permanganate used for Expts. 1—4 was found to be 1·0105*N*/10 (1·01040, 1·01061, 1·01047 in separate determinations), and that for Expts. 5—8 was 1·0084*N*/10 (1·00863, 1·00782, 1·00876).

The atomic weight was calculated from the contents of oxide and of C_2O_3 by means of the expression : atomic weight $= \left(\frac{\%\ \text{oxide}}{\%\ C_2O_3} \times 108\right) - 24.$

Determination of Oxalate, and Atomic Weight.

No.	Terbium oxalate, g.	Titration, ml.	C_2O_3, %.	Atomic weight.	No.	Terbium, oxalate, g.	Titration, ml.	C_2O_3, %.	Atomic weight.
1	0·34336	26·56	28·139	158·88	5	0·57361	44·48	28·149	158·81
2	0·32038	24·767	28·119	159·00	6	0·58153	45·08	28·141	158·86
3	0·32307	24·99	28·139	158·88	8	0·62028	48·11	28·157	158·76
4	0·56839	43·92	28·110	159·06				Mean	158·89 ± 0·04

(No. 7 gave a value 158·66, which has been rejected.) The following atomic weights were used : Na = 22·997, C = 12·00. Should the value for carbon be raised to 12·01 the value for terbium would become 158·92, but the aim of this work has been to determine only the first place of decimals and the value 158·9 is obtained. This figure is in complete accord with the work of Aston (*Proc. Roy. Soc.*, 1934, *A*, **146**, 46), who finds terbium to have only the mass number 159. The packing fraction may be expected to reduce this by about 0·08. Hence, chemical and mass-spectroscopic methods both indicate a value 158·9 for the atomic weight of terbium.

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